P/ TENT COOPERATION TREAT

	From the INTERNATIONAL BUREAU
PCT	То
NOTIFICATION OF ELECTION (PCT Rule 61.2)	Assistant Commissioner for Patents United States Patent and Trademark Office Box PCT Washington, D.C.20231 ETATS-UNIS D'AMERIQUE
Date of mailing (day/month/year) 18 August 2000 (18.08.90)	in its capacity as elected Office
International application No. PCT/US99/24013	Applicant's or agent's file reference 98-33-SE PCT
International filing date (day/month/year) 09 November 1999 (09.11.99)	Priority date (day/month/year) 12 November 1998 (12.11.98)
Applicant	12 110101111001 1000 (12.11.30)
SANDERSON, Andrew, J. et al	
1. The designated Office is hereby notified of its election made X in the demand filed with the International Preliminary 09 June 2000 (iii)	Examining Authority on: 09.06.00) ational Bureau on:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20. Switzerland

Pascat Pirrou

PATENT COOPERATION TREAT

PCT

NOTIFICATION OF RECEIPT OF RECORD COPY

(PCT Rule 24.2(a))

From the INTERNATIONAL BUREAU

To

COLTON, Kendrew, H.
Pillsbury Madison & Sutro, LLP
1100 New York Avenue, N.W.
Washington, DC 20005
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 03 May 2000 (03.05.00)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference 98-33-SE PCT	International application No. PCT/US99/24013

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

CORDANT TECHNOLOGIES, INC. (for all designated States except US) SANDERSON, Andrew, J. et al (for US)

International filing date

09 November 1999 (09.11.99)

Priority date(s) claimed

12 November 1998 (12.11.98)

Date of receipt of the record copy by the International Bureau

27 April 2000 (27.04.00)

List of designated Offices

AP:GH,GM,KE,LS,MW,SD,SL,SZ,TZ,UG,ZW

EA: AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

EP:AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SEOA:BF,BJ,CF,CG,CI,CM,GA,GN,GW,ML,MR,NE,SN,TD,TG

National :AE,AL,AM,AT,AU,AZ,BA,BB,BG,BR,BY,CA,CH,CN,CR,CU,CZ,DE,DK,DM,EE,ES,FI,GB,GD,GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KP,KR,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MN,MW,MX,NO,NZ,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,US,UZ,VN,YU,ZA,ZW

ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

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In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

X time limits for entry into the national phase

confirmation of precautionary designations

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland

J. Leitao

PITENT COOPERATION TREATIV

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COMMUNICATION OF INTERNATIONAL APPLICATIONS

(PCT Article 20)

Date of mailing.

04 May 2000 (04.05.00)

From the INTERNATIONAL BUREAU

Assistant Commissioner for Patents United States Patent and Trademark Office Box PCT Washington, D.C.20231 ETATS-UNIS D'AMERIQUE

in its capacity as designated Office

The International Bureau transmits herewith copies of the international applications having the following international application numbers and international publication numbers:

international application no.:

<u>International publication no.:</u>

PCT/US99/24013

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ITENT COOPERATION TREAT

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COMMUNICATION IN CASES FOR WHICH NO OTHER FORM IS APPLICABLE

From the INTERNATIONAL BUREAU

COLTON, Kendrew, H.
Pillsbury Madison & Sutro, LLP
1100 New York Avenue, N.W.
Washington, DC 20005
ETATS-UNIS D'AMERIQUE

Date of mailing (day month year) 04 May 2000 (04.05.00)		
Applicant's or agent's file reference	REPLY DUE	
98-33-SE PCT	see paragraph 1 below	
International application No.	International filing date (day month year)	
PCT/US99/24013	09 November 1999 (09.11.99)	
Applicant CORDANT TECH	HNOLOGIES, INC.	
1. REPLY DUE within months/days from the	above date of mailing	
NO REPLY DUE, however, see below		
MPORTANT COMMUNICATION		
INFORMATION ONLY		
2. COMMUNICATION:		
The International Bureau regrets to inform the a transmittal of the record copy, the above-referenced inte the expiration of 18 months from the priority date, as pro-	applicant that, due to the receiving Office's (RO/US) late rnational application has not been published promptly after ovided in PCT Article 21(2)(a).	
International publication will take place on 15.	June 2000 (15.06.00).	
Meanwhile, the International Bureau (WO) will each designated Office, in accordance with PCT Article	communicate a copy of the international application to	
A copy of this notification has been sent to the concerned	receiving Office (RO US) and to all designated Offices	

PCT

REQUEST

acceiving Office use only	
International Application No.	
International Filing Date	
Name of receiving Office and "PCT International Application"	

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty. Applicant's or agent's file reference 98-33-SE PCT (if desired) (12 ch. racters maximum) Box No. I TITLE OF INVENTION METHOD FOR THE SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS IN NON-HALOGENATED **SOLVENTS** Box No. II APPLICANT Name and address: (Family name followed by given name; for a legal entity, full official The address must include postal code and name of country. The country of the address indicated in this This person is also inventor. Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) CORDANT TECHNOLOGIES, INC. Telephone No. 15 West Temple, Suite 1600 Salt Lake City, Utah 84101-1532 Facsimile No. United States of America Teleprinter No. State (that is, country) of residence: State (that is, country) of nationality: US US the States indicated in the Supplemental Box all designated States all designated States except the United States This person is applicant the United States of America of America only for the purposes of: FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S) Box No. III Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this This person is: Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) SANDERSON, Andrew J. applicant only 2711 North, Mountain Road North Ogden, Utah 84414 applicant and inventor United States of America inventor only (If this check-box is marked, do not fill in below.) State (that is, country) of nationality: State (that is, country) of residence: US GB all designated States except the United States of America of America only the States indicated in all designated This person is applicant I the Supplemental Box for the purposes of: States Further applicants and/or (further) inventors are indicated on a continuation sheet. AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE Box No. IV The person identified below is hereby/has been appointed to act on behalf common representative agent of the applicant(s) before the competent International Authorities as: Name and address: (Family name followed by given name; for a legal entity, full official Telephone No

The second section is a second second	
Washington, D.C. 20005	
United States of America	Teleprinter No
1 3 Address for correspondence M.	

Sheet No. . . . Z....

	xes is used, this sheet is not to be included in the request.
ame and address: (Family name followed by given name: for enderess must include postal code and name of country. To it is the applicant's State (that is, country) of residence if no DWARDS, Wayne 00S 610 West remonton, Utah 84337 Inited States of America	he country of the address indicated in this, This person is:
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Name and address: (Family name followed by given name:)	for a legal entity, full official designation. The country of the address indicated in this of State of residence is indicated below.) This person is: applicant only applicant and inventor inventor only (If this check-box)
Name and address: (Family name followed by given name;) the address must include postal code and name of country. Store is the applicant's State (that is, country) of residence if no State (that is, country) of nationality. This person is applicant all designated all designated	for a legal entity, full official designation. The country of the address indicated in this of State of residence is indicated below.) This person is: applicant only applicant and inventor inventor only (If this check-box is marked, do not fill in below.)
Name and address: (Family name followed by given name; is the address must include postal code and name of country. Stox is the applicant's State (that is, country) of residence if no state (that is, country) of nationality. This person is applicant all designated	for a legal entity, full official designation. The country of the address indicated in this of State of residence is indicated below.) This person is: applicant only applicant and inventor inventor only (If this check-box is marked, do not fill in below.) State (that is, country) of residence: It designated States except of America only the States indicated in the United States of America only the Supplemental Boy of a legal entity, full official designation. The country of the address indicated in this This person is:
State (that is, country) of nationality. This person is applicant all designated all for the purposes of: Name and address: (Family name followed by given name: It is provided to the purposes of: Name and address: (Family name followed by given name: It is not name of country.)	This person is: applicant only applicant and inventor inventor only (If this check-box is marked, do not fill in below.) State (that is, country) of residence: It designated States except the United States of America only the Supplemental Boy for a legal entity, full official designation This person is: applicant only inventor only (If this check-box is marked, do not fill in below.) State (that is, country) of residence: The Country of the address indicated in this the Supplemental Boy for a legal entity, full official designation The country of the address indicated in this to State of residence is indicated below.) applicant only This person is:

The following designations are hereby made under Kule 4.9(a) (mark the applicable check-boxes; at least one must be marked): AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Cote d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line) National Patent (if other kind of protection or treatment desired, specify on dotted line): LR Liberia United Arab Emirates \boxtimes Lesotho ALAlbania LT Lithuania AMArmenia X LU Luxembourg ΑT Austria \boxtimes LV Latvia \mathbf{AU} Australia MD Republic of Moldova \mathbf{X} AZAzerbaijan \boxtimes BABosnia and Herzegovina MG Madagascar \boxtimes BBBarbados MK The former Yugoslav Republic of Macedonia \boxtimes BGBulgaria \boxtimes BRMN Mongolia \boxtimes MW Malawi BYBelarus \boxtimes MX Mexico CACanada NO Norway CH and LI Switzerland and Liechtenstein X X NZ New Zealand CN China X PL Poland CUCzech Republic CZPT Portugal DE Germany RO Pomania X DK RU Eussian Federation Denmark EE SD Sudan Estonia \times SE -> weden $\mathbf{E}\mathbf{S}$ Spain XSG Singapore FI SI GBSlovenia United Kingdom SK Slovakia GD Grenada GE SL Sierra Leone Georgia X TJ Tajikistan GH Ghana \boxtimes TM Turkmenistan GMGambia HRCroatia TT Trimidad and Tobago HU Hungary ID UA Ukraine Indonesia $\mathbf{U}\mathbf{G}$ Uganda Π L Israel

A Section X Means

UZ Uzbekistan

YU Yugoslavia

US United State of America

VN Viet Nam

ZA South Africa

Precautionary Designation Statement: in a 14% of the designation, made above, the applicant also make under Rule 4.9(4) all other designations which would be permitted under the Ps. Levcept any designations) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declare that those additional designations are subject to confirmation and the confirmation are confirmation and the confirmation are confirmation and the confirma

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India

Iceland

Japan

Kenya

Democratic People's Republic of Korea

- 1. If, in any of the Boxes, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No. ..." [indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:
 - if more than two persons are involved as applicants and/or inventors and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
 - if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is
 - if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and next to (each) name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or ()API patent) for the purposes of which the named person is inventor;
 - if, in addition to the agent(s) indicated in Box IV, there are further agents: in such case, write "Continuation of Box No IV" and indicate for each further agent the same type of information as required in Box No. IV:
 - if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "patent of addition," or "certificate of uddition," or if, in Box No. V., the name of the United States of America is accompanied by an indication "continuation" or "continuation-in-part": in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
 - if, in Box No. VI, there are more than three earlier applications whose priority is claimed: in such case, write "Continuation (vi) of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI:
 - if, in Box No. VI, the earlier application is an ARIPO application: in such case, write "Continuation of Box No VI", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris (vii) Convention for the Protection of Industrial Property for which that earlier application was filed.
 - 2. If, with regard to the precautionary designation statement contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement in such case, write "Designation()) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.
 - If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning non-prejudicial disclosures or exceptions to lack of novelty: in such case, write "Statement concerning non-prejudical disclosures or exceptions to lack of novelty" and furnish that statement below

Box No. iV. Agent or Common Representative: (continued)

EDGELL, G. Paul BIRD, Donald J. KOKULIS, Paul N. ECCLESTON, Lynn E. JAF.OPIN, David A LIPPITT Raymond F. GOWDEY Peter W. PAULSON, Mark G. KNIGHT, G. Lloyd LAZAR, Dale S. KLIMA, Timothy J. LOVE, Carl G. PERRY, Glenn J. McQUADE Paul F MARTIN, Edgar H. DZWONCZYK, Michael R MORDUCH, Ruth N. WHITE, Paul E., Jr. SIRILLA, George M. JOYCE, Kevin E. BENGTSSON, W. Patrick BARUFFA, Jacks. WISE, Roger R.

SMYRSKI, Steven W KIRKPATRICK, Anita M. ZAITLEN, Richard H.

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GLAZIER, Stephen C. HESS, Adam R.

FINEELSTEIN, Jay M. NAGY, Paul G.

All attorneys are partners of the firm of PILLSBURY MADISON & SUTRO, LLP. The address, telephone number, and

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Filing data			claims are indicated in t	
Filing date	Number	V	Vhere earlier application	is:
of earlier application (day/month/year)	of earlier application	national application: country	regional application:* regional Office	international application receiving Office
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em (3)				
All of the earlier applicate	s requested to prepare and ion(s) (only if the earlier is international application ARIPO application, it is mandate thich that earlier application was fi	application was filed with is the receiving Office) ide ors to indicate in the Supplementa	the Office which for the ntified above as item(s): Box at least one country par	<i>ie</i> (1)
Box No. VII INTERNAT	TIONAL SEARCHING A	UTHORITY		
Choice of International Searchi If two or more International competent to carry out the intern- uthority chosen; the two-letter of	ng Authority (ISA) Searching Authorities are ational search, indicate the	Request to use results of e search has been carried out by Date (day/month/year)	or requested from the Internati	
ISA/EP				
Box No. VIII CHECK LI	IST: LANGUAGE OF FI			
This international application the following number of she		onal application is accompulation sheet	anied by the item(s) man	ked below:
request :	<u> </u>	e signed power of attorney		
description (excluding)	3. ☐ copy of	general power of attorney;	reference number, if any	y:
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FEE CALCULATION SHEET

	For receiving Office use only	
al applic	cation No.	

Annex to	the Request	International application No.	
		_[
Applicant's or agent's file reference	98-33-SE PCT	Date stamp of the receiving Office	
Applicant			
CORDANT TECHNOLOGIE	S, INC.		
CALCULATION OF PRESCI	RIBED FEES		
1. TRANSMITTAL FEE		240.00 _T	
2. BEILICHTEE		1,002.00 S	
International search to be car		netent in relation to the international	
(If two or more Internation application, indicate the name	nat searching Authorities are comp ne of the Authority which is chosen to	petent in relation to the international carry out the international search.)	
3. INTERNATIONAL FEE			
Basic Fee			
The international application	contains 41 sheets.		
first 30 sheets		455.00 b ₁	
	510.00 =	110.00 b ₂	
remaining sheets addition	onal amount		
Add amounts entered at b 1	and b $_2$ and enter total at B $_2$	565.00 B	
Designation Fees	ΔΙΙ		
The international application 10	n contains ALL designations.	1,050.00 D	
number of designation fees	amount of designation fee		
payable (maximum 10)			
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(Applicants from certain State	es are entitled to a reduction of 75% o	of the	
international fee. Where the a the total to be entered at I is 2:	applicant is (or all applicants are) so ent 5% of the sum of the amounts entered at I	B and	
4. FEE FOR PRIORITY DOC	'UMENT (if applicable)	: : : : 15.00 P	
5. TOTAL FEES PAYABLE		2,872.00	
Add amounts entered at T,	S, I and P, and enter total in the TOT	AL box TOTAL	
The designation fees are	not paid at this time.		
MODE OF PAYMENT			1
authorization to charge deposit account (see bel	low) ank draft	coupons	
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V3-39 <i>1</i> 5	09 November 199		· · · · · · · · · · · · · · · · · · ·
Deposit Account Number	Date (day month year)	Signature Lendrew H. Co	olton

Form PCT/RO/101 (Annex) (January 1999)

Legalistic 1989 Fore Politike See Notes to the fee calculation sheet

The demand must be filed directly .th the competent International Preliminary examin. Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/ _EP

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:

The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

Identification of IPEA		Date of receipt of D	EMAND
Box No. I IDENTIFICATION C	OF THE INTERNATIONAL A	PPLICATION	Applicant's or agent's file reference 98-33-SE PCT
International application No.	International filing date	(day/month/year)	(Earliest) Priority date (day/month/year)
PCT/US99/24013	09 November 1999	(09.11.99)	12 November 1998 (12.11.98)
Title of invention METHOD FOR THE SYNTHESIS SOLVENTS	OF ENERGETIC THERMOR	PLASTIC ELASTON	MERS IN NON-HALOGENATED
Box No. II APPLICANT(S)			
	address must include postal code a	al entity, full official ad name of country.)	Telephone No.:
CORDANT TECHNOLOGIES, INC. 15 West Temple, Suite 1600 Salt Lake City, Utah 84101-1532 United States of America			Facsimile No.:
			Teleprinter No.:
State (that is, country) of nationality US	:	State (that is, country US	y) of residence:
Name and address: (Family name foliname of country.) SANDERSON, Andrew J. 2711 North, Mountain Road North Ogden, Utah 84414 United States of America	lowed by given name; for a legal e	ntity, full official design	nation. The address must include postal code an
State (that is, country) of nationality US		State (that is, country US	y) of residence:
Name and address: (Family name followment of country.) EDWARDS, Wayne 600S 610 West Trementor Wish 94227	lowed by given name; for a legal e	entity, full official desig	nation. The address must include postal code an
State (that is, country) of nationality		State (that is, countr	y) of residence:

Sheet No. .2.

International application No. PCT/US99/24013

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CO	DRRESPONDENCE	
The following person is agent common representative		
and has been appointed earlier and represents the applicant(s) also for international preliminary examination.		
is hereby appointed and any earlier appointment of (an) agent(s) /common rep	resentative is hereby revoked.	
is hereby appointed, specifically for the procedure before the International Proaddition to the agent(s)/common representative appointed earlier.	eliminary Examining Authority, in	
Name and address: (Family name followed by given name: for a legal entity, full official designation	Telephone No.:	
The address must include postal code and name of country.) COLTON, Kendrew H.	202 861-3000	
PILLSBURY MADISON & SUTRO, LLP	Facsimile No.:	
1100 New York Avenue, NW	202 822-0944	
Washington, DC 20005 United States of America		
	Teleprinter No.:	
Address for correspondence: Mark this check-box where no agent or common the space above is used instead to indicate a special address to which correspond	representative is/has been appointed and dence should be sent.	
Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION		
Statement concerning amendments:*		
1. The applicant wishes the international preliminary examination to start on the basis of	:	
the international application as originally filed		
the description as originally filed		
as amended under Article 34		
the claims as originally filed		
as amended under Article 19 (together with any accompa	nying statement)	
as amended under Article 34		
the drawings as originally filed		
as amended under Article 34		
2. The applicant wishes any amendment to the claims under Article 19 to be cor	sidered as reversed.	
The applicant wiches the start of the international preliminary examination to		
months from the priority date unless the International Preliminary Exam amendments made under Article 19 or a notice from the applicant that he described (Rule 69.1(d)). (This check-box may be marked only where the time limit under Where no check-box is marked, international preliminary examination will start on originally filed or, where a copy of amendments to the claims under Article 19 application under Article 34 are received by the International Preliminary Examinin a written opinion or the international preliminary examination report, as so amended	ning Authority receives a copy of any oes not wish to make such amendments der Article 19 has not yet expired.) the basis of the international application as and/or amendments of the international g Authority before it has begun to draw up	
Language for the purposes of international preliminary examination: English		
which is the language in which the international application was filed.		
which is the language of a translation furnished for the purposes of internation	nal search.	
BOX NO A PERCUION OF STATES	() man () () () ()	
The applicant hereby elects all eligible States (that is, all States which have been designate	d and which are bound by Chapter II of the	
PCT)	a contract and a contract of some poor in significant	
ex to fine the CH except State. Alpah the applicant is the not to elect		

Sheet No. .3.

International application No.

PCT/US99/24013

Box	No. VI CHECK LIST					
Th Bo	te demand is accompanied by the following on No. IV, for the purposes of international pro-	elements, in the	ne language nination:	referred to in	Examining .	tional Preliminary Authority use only
1.	translation of international application	:		sheets	received	not received
2.	amendments under Article 34	:		2 sheets		
3.	copy (or, where required, translation) of amendments under Article 19			she e ts]		
4.	copy (or, where required, translation) of statement under Article 19			sheets		
5.	letter			1 sheets		
6.	other (specify)	:		sheets		
— The	demand is also accompanied by the item(s) m	arked below:	5			
1.	fee calculation sheet		4.	statement ex	plaining lack of sign	ature
2.	separate signed power of attorney		5.	nucleotide a	nd or amino acid seq	uence listing in
3.	copy of general power of attorney; reference number, if any:		6.	·	(y): Receipt	
Rox	: No. VII SIGNATURE OF APPLICAL	NT. AGENT	OR COM	MON REP	RESENTATIVE	
Ker	Audithan Andrew H. Colton					
1.	For International Date of actual receipt of DEMAND:	onal Prelimina	ary Examini	ng Authority u	se only	
2.	Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):					
3.	The date of receipt of the demand is A from the priority date and item 4 or 5,			9 months		cant has been accordingly.
	EXCUSED pursuant to Rule 82	nagi mere			a	ie, ine delaj disait was i
		For Internation	onal Burea	ı use only —		
	ere e (# 1 g)					

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FEE CALCULATION SHEET

Annex to the Demand for international preliminary examination

		For International Preliminary Examining Authority use only
International application No.	PCT/US99/24013	To memanona Fromman Branch graduotity use omy
Applicant's or agent's file reference	98-33-SE PCT	Date stamp of the IPEA
Applicant CORDANT TECHNOLOG	IES, INC.	
Calculation of prescribed	fees	
1. Preliminary examination	1 fee	2,998.29 P
entitled to a reduction Where the applicant is entitled, the amount to handling fee.)	ants from certain States are of 75% of the handling fee. s (or all applicants are) so be entered at H is 25% of the	287.51 H
 Total of prescribed fees Add the amounts entere and enter total in the TC 	d at P and H OTAL box	3,285.80
		TOTAL
Mode of Payment		
authorization to cha	arge deposit EA (see below) cash	
cheque	revenue	e stamps
postal money order	coupon	S
bank draft	other (s	pecify):
Deposit Account Authoriz	eation (this mode of payment may no	t be available at all IPEAs)
The IPEA .		a total fan (in 18 igta k ik is a t - ins - kan (it) - inst
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	09 June 2000	Bull to Co
Part I I I I A b A Annua	ate again nata a 2	en e



INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or a	gent's file reference	FOR FURTHER see Notification of (Form PCT ISA/2	of Transmittal of International Search Report (20) as well as, where applicable, item 5 below.
International ap		International filing date (day, month year)	(Earliest) Priority Date (day, month, year)
PCT/US 99	/ 24013	09/11/1999	12/11/1998
Applicant			
CORDANII	ECHNOLOGIES, INC	. et al.	
according to A	urticle 18. A copy is being tri onal Search Report consists	n prepared by this International Searching Autansmitted to the International Bureau. of a total of 2 sheets. a copy of each prior art document cited in this	
	t he report egard to the language , the	international search was carried out on the ba	sis of the international application in the
langua	age in which it was filed, un	less otherwise indicated under this item.	
	the international search w Authority (Rule 23.1(b)).	vas carried out on the basis of a translation of	the international application furnished to this
b. With r	regard to any nucleotide ar arried out on the basis of th	nd/or amino acid sequence disclosed in the in esequence listing:	nternational application, the international search
		onal application in written form.	
	filed together with the inte	ernational application in computer readable for	m.
	furnished subsequently to	o this Authority in written form.	
$\overline{\Box}$	furnished subsequently to	this Authority in computer readble form.	
	the statement that the su international application a	bsequently furnished written sequence listing oas filed has been furnished.	does not go beyond the disclosure in the
	the statement that the inf furnished	ormation recorded in computer readable form	is identical to the written sequence listing has been
2	Certain claims were fou	ind unsearchable (See Box I)	
3	Unity of invention is lad	king (see Box II)	
4 With rega	rd to the title.		
	the text is approved as si	ubmitted by the applicant	
		shed by this Authority to read as follows:	
METHO SOLVE	D FOR THE SYNTHE	SIS OF THERMOPLASTIC ELASTO	MERS IN NON-HALOGENATED
5 With rega	ard to the abstract .		
	arawings and a	tedat e dita	
	as suggested by the app	isant	🔙 ो 🦠 🐧 और एके of the figures
	pecause the applicant fa	iled to suggest a figure	
_		1	

INTERNATIONAL SEARCH REPORT

International Application No S 99/24013

a. classification of subject matter IPC 7 C08G18/48 C08G C08G18/08 C08G18/76

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched. (classification system followed by classification symbols)

C08G C06B IPC 7

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

4 June 1997 (1997-06-04) claims; examples US 5 210 153 A (MANSER ET AL) 11 May 1993 (1993-05-11) column 6, line 27 - line 36; claims 1.7; examples 12-21, 30-33	C. DOCUM	ENTS CONSIDERED TO BE RELEVANT	
4 June 1997 (1997-06-04) claims; examples US 5 210 153 A (MANSER ET AL) 11 May 1993 (1993-05-11) column 6, line 27 - line 36; claims 1.7; examples US 4 806 613 A (WARDLE) 21 February 1989 (1989-02-21)	Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A US 5 210 153 A (MANSER ET AL) 11 May 1993 (1993-05-11) column 6, line 27 - line 36; claims 1,7; examples A US 4 806 613 A (WARDLE) 21 February 1989 (1989-02-21) 1-3, 12-21,	А	4 June 1997 (1997-06-04)	12-21,
examples US 4 806 613 A (WARDLE) 21 February 1989 (1989-02-21) 1-3, 12-21,	A	US 5 210 153 A (MANSER ET AL) 11 May 1993 (1993-05-11)	15-21,
	Α	examples US 4 806 613 A (WARDLE) 21 February 1989 (1989-02-21)	12-21,

Further documents are listed in the continuation of box C

X

Patent family members are listed in annex

Special nategories of cited documents.

- A lidocument defining the general state of the lart which is not considered to be of particular relevance.
- °Е." earlier document but published on or after the international filling date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- document referring to an oral disclosure, use Lexhibition or other means
- T" later document published after the international filing date or priority date and not in conflict with the Japplication but cited to understand the principle or theory, underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is ltaken alone
- "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive latep when the document is combined with one or more other, such documents, such combination being obvious to all person skilled

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11. 09, 2000

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र प्रात्मकत्वत शुक्रकतर (स. क. शिद्धाः प्रशंस शिक्षकारातुन्तः)

A pellegang House

INTERNATIONAL SEARCH REPORT

nform on patent family members

International Application No
P 99/24013

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2307688	Α	04-06-1997	NONE	
US 5210153	Α	11-05-1993	NONE	
US 4806613	Α	21-02-1989	CA 1318052 A DE 68928734 D DE 68928734 T EP 0335499 A JP 2014216 A JP 2705821 B	18-05-1993 20-08-1998 21-01-1999 04-10-1989 18-01-1990 28-01-1998



RECO

REQUEST

The undersigned requests that the present

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PCT ROD

international application be processed according to the Patent Cooperation Treaty.

International Parties No. 9 / 24013

(09.11.99)

International Filing Date

0 9 NOV 1999

ng Office use only

PCT INTERNATIONAL
NAME PLICATION ROLLS
ional Application"

Applicant's or agent's file reference

98-33-SE PCT

		(if desired) (12 character	rs maximum)
Box No. I METHOD FO SOLVENTS	TITLE OF INVENTION R THE SYNTHESIS OF ENERGETIC THERMO	OPLASTIC ELASTOMI	ERS IN NON-HALOGENATED
Box No. II	APPLICANT		
The address mus Box is the application CORDANT T	ess: (Family name followed by given name; for a tinclude postal code and name of country. The country ant's State (that is, country) of residence if no State of res	or the aggress maiculed in i	This person is also inventor. Telephone No.
15 West Tem Salt Lake City United States	nple, Suite 1600 y, Utah 84101-1532 s of America		Facsimile No.
			Teleprinter No.
State (that is, o	country) of nationality:	State (that is, country) US	
This person is for the purpose	es of: States the United S	tates of America o	the United States the States indicated in the Supplemental Box
Box No. III	FURTHER APPLICANT(S) AND/OR (FURT	THER) INVENTOR(S)	
SANDERSO 2711 North,	st include postal code and hank of country) from the country of residence if no State of re. N, Andrew J. Mountain Road I, Utah 84414 Is of America		applicant only applicant and inventor inventor only (If this check-box is marked, do not fill in below.)
State (that is,	country) of nationality:	State (that is, country US) of residence:
This person is for the purpos	s applicant all designated all designated ses of: applicants and/or (further) inventors are indicated or	d States except tates of America	he United States the States indicated in the Supplemental Box
Further a			CORRESPONDENCE
Box No. IV	AGENT OR COMMON REPRESENTATIV		CORRESTON
	dentified below is hereby/has been appointed to act of ant(s) before the competent International Authorities	. A\	agent common representative
Name and ad-	dress: (Family name followed by given name; for designation. The address must include postal	 a legal entity, full off- code and name of count 	(Cial) Telephone No. (202 861 3000)
Fashington	es of America		Leteprinter Sc
Addre	ss for correspondence M		and and the second seco



PET/US 99/24013

Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTOR(S)							
If none of the following sub-boxes is used, this sheet is not to be included in the request.							
Name and address: (Family name followed by given name; for a legal en The address must include postal code and name of country. The country Box is the applicant's State (that is, country) of residence if no State of resid	of the address indicated in this	This person is: applicant only applicant and inventor inventor only (If this check-box is marked, do not fill in below.)					
State (that is, country) of nationality: US	State (that is, country) of US	residence:					
This person is applicant all designated for the purposes of:		nited States the States indicated in the Supplemental Box					
Name and address:(Family name followed by given name; for a legal en The address must include postal code and name of country. The country Box is the applicant's State (that is, country) of residence if no State of res	of the address indicated in this	This person is: applicant only applicant and inventor inventor only (If this check-box is marked, do not fill in below.)					
State (that is, country) of nationality:	State (that is, country) of	residence:					
This person is applicant all designated all designated for the purposes of:		nited States the States indicated in the Supplemental Box					
Name and address: (Family name followed by given name; for a legal en The address must include postal code and name of country. The country Box is the applicant's State (that is, country) of residence if no State of res	of the address indicated in this	This person is: applicant only applicant and inventor inventor only (If this check-box is marked, do not fill in below.)					
State (that is, country) of nationality:	State (that is, country) of	residence:					
		nited States the States indicated in the Supplemental Box					
Name and address: (Family name followed by given name: for a legal en The address must include postal code and name of country. The country Box is the applicant's State (that is, country) of residence if no State of res	of the address indicated in this	This person is: applicant only applicant and inventor					
$S_{i,i} \subset \mathcal{D}_{i,i}$, $\mathcal{D}_{i,i}$, $\mathcal{D}_{i,i}$ and \mathcal{D}_{i}	State (2001) (2002) 34	residence					
This person is applicant all designated all designated	I States except the U	nited States the States indicated in					

DESIGNATION OF FS Box No.V

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- EP European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Cote d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

\boxtimes	\mathbf{AE}		\boxtimes		Liberia
\boxtimes	\mathbf{AL}		\boxtimes	LS	Lesotho
\boxtimes	\mathbf{AM}	Armenia	\times		Lithuania
\boxtimes	ΑT	Austria	\boxtimes	LU	Luxembourg
\boxtimes	$\mathbf{A}\mathbf{U}$	Australia	\boxtimes		Latvia
\boxtimes	AZ	Azerbaijan	\times	MD	Republic of Moldova
\boxtimes	BA	Bosnia and Herzegovina	\boxtimes	MG	Madagascar
\boxtimes	BB	Barbados	\mathbf{X}		The former Yugoslav Republic of Macedonia
\boxtimes	BG	Bulgaria			
\boxtimes	BR	Brazil	\boxtimes	MN	Mongolia
\boxtimes	BY	Belarus	\boxtimes	MW	Malawi
\boxtimes	CA	Canada	\boxtimes	MX	Mexico
\boxtimes	CH a	nd LI Switzerland and Liechtenstein	\boxtimes	NO	Norway
\boxtimes	CN	China	\boxtimes	NZ	New Zealand
\boxtimes	CU	Cuba	\times	PL	Poland
\boxtimes	CZ	Czech Republic	\boxtimes	PT	Portugal
\times	DE	Germany	\boxtimes	RO	Romania
\boxtimes	DK	Denmark	\boxtimes	RU	Russian Federation
\times	EE	Estonia	\boxtimes	SD	Sudan
\boxtimes	ES	Spain	\boxtimes	SE	Sweden
\boxtimes	FI	Finland	\boxtimes	SG	Singapore
\boxtimes	GB	United Kingdom	\boxtimes	SI	Slovenia
\boxtimes	GD	Cirenada	\boxtimes	SK	Slovakia
\boxtimes	GE	Georgia	\boxtimes	SL	
\boxtimes	GH	Ghana	\boxtimes	TJ	Tajikistan
\boxtimes	GM	Gambia	\boxtimes		Turkmenistan
\boxtimes	HR	Croatia	\boxtimes		Turkey
\boxtimes	HU	Hungary	\boxtimes		Trinidad and Tobago
\boxtimes	ID	Indonesia	\times		Ukraine
\boxtimes	11.	Israel	\mathbf{X}		Uganda
\boxtimes	IN	India	\boxtimes	US	United States of America
\boxtimes	IS	Iceland	_		
\boxtimes	JP	Japan	\boxtimes		Uzbekistan
\boxtimes	KE	Kenya	\boxtimes	_	Viet Nam
\boxtimes	KG	Kyrgyzstan	\boxtimes		Yugoslavia
\boxtimes	KP	Democratic People's Fepublic of Korea	\boxtimes		South Africa
		<u></u>	\times		V Zimbabwe
\boxtimes	KR	Republic of Koren	Ch:	eck-b	oves reserved for design time States or but they a feet and

Elecautionary Designation Statemers

and the first of the state of the second and the second of other designations which would be permitted under the PCI except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and 1 that any designation which is not continued but to the purple of 15 months from the project discount to be easily but a set to

CT/US 99/24013

Supplemental Box

If the Supplemental Box is not used, this sheet need not be included in the request.

1. If, in any of the Boxes, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No. ..."

[indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:

- (i) if more than two persons are involved as applicants and/or inventors and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
- (ii) if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Box No. III" and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
- (iii) if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No. II" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
- (iv) If, in addition to the agent(s) indicated in Box IV, there are further agents: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV:
- (v) If, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "patent of addition," or "certificate of addition," or if, in Box No. V., the name of the United States of America is accompanied by an indication "continuation" or "continuation-in-part": in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
- (vi) if, in Box No. VI, there are more than three earlier applications whose priority is claimed: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI:
- if, in Box No. VI, the earlier application is an ARIPO application: in such case, write "Continuation of Box No. VI", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed.
- 2. If, with regard to the precautionary designation statement contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.
- 3. If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning non-prejudicial disclosures or exceptions to lack of novelty; in such case, write "Statement concerning non-prejudical disclosures or exceptions to lack of novelty" and furnish that statement below.

Box No. iV. Agent or Common Representative: (continued)

KOKULIS, Paul N. LIPPITT, Raymond F. KNIGHT, G Lloyd LOVE, Carl G. MARTIN, Edgar H. BIRD, Donald J.
ECCLESTON, Lynn E.
GOWDEY Peter W.
LAZAR, Dale S.
PERRY, Glenn J.

EDGELL, G. Paul JAKOPIN, David A. PAULSON, Mark G. KLIMA, Timothy J. McQUADE. Paul F. DZWONCZYK, Michael R.

MORDUCH, Ruth N
JOYCE, Kevin E.
WISE, Roger R.
ZAITLEN, Richard H.
MORDUCH, Ruth N
WHITE, Paul E., Jr.
BENGTSSON, W. F
SMYRSKI, Steven W

WHITE, Paul E., Jr. SIRILLA, George M. BENGTSSON, W. Patrick BARUFKA, J ack s. SMYRSKI, Steven W KIRKPATRICK, Anita M.

HESS, Adam R. GLAZIER, Stephen C.

FINKELSTEIN, Jay M. NAGY, Paul G.

All attorneys are partners of the firm of PILLSBURY MADISON & SUTRO, LLP. The address, telephone number, and facsimile number of all the above attorneys are as indicated in Box IV

PCT/US 99/24013

Box No. VI PRIORITY C		Further priority	clar e indicated in t	he Supplemental Box.			
Filing date	Number	Where earlier application is:					
of earlier application (day/month/year)	of earlier application	national application: country	regional application:* regional Office	international application: receiving Office			
item (1) 12/November/1998 (12/11/98)	60/108,455	US					
item (2)							
item (3)							
of the earlier application	requested to prepare and tron(s) (only if the earlier a international application i. RIPO application, it is mandatory ich that earlier application was file	pplication was filed with s the receiving Office) idet s to indicate in the Supplemental	the Office which for the ntified above as item(s): Box at least one country part	e			
Box No. VII INTERNATI	ONAL SEARCHING AU	THORITY					
Choice of International Searching (if two or more International Searching) competent to carry out the internal Authority chosen; the two-letter cou	earching Authorities are invalid in a control in a contro	Request to use results of ea search has been carried out by a Date (day/month/year)	or requested from the Internatio				
ISA/=P							
	T: LANGUAGE OF FILE						
This international application of the following number of sheet		nal application is accompa ation sheet	nied by the item(s) marl	ced below:			
request :		igned power of attorney					
description (excluding) sequence listing part) :	07	eneral power of attorney; resplaining lack of signature.		:			
claims :		ocument(s) identified in B	ox No. VI as items(s):				
abstract :		n of international applicati					
drawings	· · · · · · · · · · · · · · · · · · ·	- ·		r other biological material			
sequence listing part of description	<u></u>	e and/or amino acid seque ecify): Transmittal letter		eadable form			
Total number of sheets:	41						
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METHOD FOR THE SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS IN NON-HALOGENATED SOLVENTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

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This invention relates to a method of synthesizing energetic thermoplastic elastomers which are useful as binders of high energy compositions, such as rocket motor propellants, gun propellants, explosive munitions, gas generants of vehicle supplemental restraint systems, or the like.

2. Description of the Related Art

Solid high energy compositions, such as propellants, explosives, gas generants, and the like comprise solid particulates, such as fuel particulates and/or oxidizer particulates, dispersed and immobilized throughout a polymeric binder matrix.

Conventional solid composite propellant binders utilize cross-linked elastomers in which prepolymers are cross-linked by chemical curing agents. As outlined in detail in U.S. Patent No. 4,361,526, there are important disadvantages to using cross-linked elastomers as binders. Cross-linked elastomers must be cast within a short period of time after addition of the curative, which time period is known as the "pot life". Disposal of a cast, cross-linked propellant composition is difficult, and usually is accomplished by burning, which poses environmental problems. Furthermore, current state-of-the-art propellant compositions have serious problems that include their use of nonenergetic binders which have lower performance and high end-of-mix viscosities.

In view of the inherent disadvantages associated with the use of cross-linked elastomeric polymers as binder materials, there has been considerable interest in developing thermoplastic elastomers suitable as binders for solid, high energy

being processible below about 120°C, it being desirable that a thermoplastic elastomeric polymer for use as a binder in a high energy system have a melting temperature of between about 60°C and about 120°C. The melting temperature is desirably at least about 60°C because the propellant composition may be subject to somewhat elevated temperatures during storage and transport, and significant softening of the propellant composition at such elevated temperatures is unwanted. The setting of the melting temperature at not more than about 120°C is determined by the instability, at elevated temperatures, of many components which ordinarily go into high energy compositions, particularly oxidizer particulates and energetic plasticizers. Many thermoplastic elastomers exhibit high melt viscosities which preclude high solids loading and many show considerable creep and/or shrinkage after processing. Thermoplastic elastomers typically obtain their thermoplastic properties from segments that form glassy domains which may contribute to physical properties adverse to their use as binders. Crosslinkable thermoplastic elastomers are block copolymers with the property of forming physical cross-links at predetermined temperatures. One thermoplastic elastomer, e.g., Kraton, brand TPE, obtains this property by having the glass transition point of one component block above room temperature. At temperatures below 109°C, the glassy blocks of Kraton form glassy domains and thus physically cross-link the amorphous segments. The strength of these elastomers depends upon the degree of phase separation. Thus, it remains desirable to have controlled, but significant, immiscibility between the two types of blocks, which is a function of their chemical structure and molecular weight. On the other hand, as the blocks become more immiscible, the melt viscosity increases, thus having a deleterious effect on the processibility of the material.

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Above-mentioned U.S. Patent No. 4,361,526 proposes a thermoplastic elastomeric binder which is a block copolymer of a diene and styrene, the styrene blocks providing a meltable crystal structure and the diene blocks imparting rubbery

processed with a volative organic solvent. Solvent processing is undesirable inasmuch as the dissolved composition cannot be cast in a conventional manner, e.g., into a rocket motor casing. Furthermore, solvent-based processing presents problems with respect to removal and recovery of solvent.

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The preparation of energetic thermoplastic elastomers prepared from polyoxetane block copolymers has been proposed in U.S. Patent No. 4,483,978 to Manser and U.S. Patent No. 4,806,613 to Wardle ("the '613 patent"), the complete disclosures of which are incorporated herein by reference to the extent that these disclosures are compatible with this invention. According to the latter, these materials overcome the disadvantages associated with conventional cross-linked elastomers such as limited pot-life, high end-of-mix viscosity, and scrap disposal problems.

The thermoplastic materials proposed by the '613 patent involve elastomers having both (A) and (B) blocks, each derived from cyclic ethers, such as oxetane and oxetane derivatives and tetrahydrofuran (THF) and tetrahydrofuran derivatives. The monomer or combination of monomers of the (A) blocks are selected for providing a crystalline structure at usual ambient temperatures, such as below about 60°C, whereas the monomer or combination of monomers of the (B) blocks are selected to ensure an amorphous structure at usual ambient temperatures, such as above about ensure an amorphous structure at usual ambient temperatures, such as above about ensure an amorphous structure at usual ambient temperatures, such as above about ensure an amorphous structure at usual ambient temperatures, such as above about ensure an amorphous structure at usual ambient temperatures, such as above about ensure an amorphous structure at usual ambient temperatures, such as above about ensure an amorphous structure at usual ambient temperatures, such as above about ensure as above about ensure an amorphous structure at usual ambient temperatures, such as above about ensure as above about ensure an amorphous structure at usual ambient temperatures, such as below about 60°C,

Typical of these materials is the random block copolymer (poly(3
azidomethyl-3-methyloxetane)-poly(3,3-bis(azidomethyl)oxetane), also known as azidomethyl-3-methyloxetane)-poly(3,3-bis(azidomethyl)oxetane), also known as azidomethyl-3-methyloxetane)-poly(3,3-bis(azidomethyl)oxetane), also known as azidomethyl-3-methyloxetane)-poly(3,3-bis(azidomethyl)oxetane), also known as azidomethyl-3-methyloxetane)-poly(4MMO/BAMO). These block copolymers have good energetic and mechanical properties. Additionally, the block copolymers can be processed without solvents to serve as binders in high performance, reduced vulnerability explosive, propellant, and gas generant formulations. Advantageously, the block copolymers conbelled to the action of the correction of the correction of

the processing techniques disclosed in the '978 and '613 patents

drawbacks have been associated with the use of the halogenated solvents disclosed in the '978 and '613 patents. One drawback is the detrimental impact that halogenated solvents have on the environment. Another drawback of halogenated solvents is attributable to the additional drying steps which the pre-polymer block are subject to after there formation. The pre-polymer blocks are typically dried either with chemical drying agent, e.g., desiccants followed by filtration or by the azeotropic removal of water. The azeotropic removal of water is performed with toluene, which is different from the solvent selected for linking the pre-polymer blocks. The performance of an additional drying step and the use of different solvents in the azeotropic drying step and the linking step complicates processing and increases overall processing time. Moreover, toluene does not completely dissolve the end-capped blocks prior to the linking reaction and can interfere with the end-capping and linking catalysts. Yet another drawback associated with halogenated solvents is the relatively low concentrations of pre-polymer blocks and linking compounds that may be loaded in halogenated solvents for processing. The loading of the thermoplastic elastomer ingredients is limited by the solubility of the ingredients in the solvent. For example, the currently used process for forming thermoplastic elastomers by linking energetic polyether diols and diisocyanates typically use approximately 30-40% by weight solutions of the reactants in dichloromethane and 0.1% by weight tin catalyst. Additionally, completion of the reaction in halogenated solvents typically takes several days to a week.

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United States Patent No. 4,393,199 to Manser describes the use of a non-halogenated solvent, nitromethane, during cationic polymerization of cyclic ethers. However, it has been found that cyclic ether pre-polymer blocks are not sufficiently soluble in nitromethane to adequately link the pre-polymer blocks once they are formed.

It would therefore be a significant advancement in the art to provide a

drawbacks associated with halogenated solvents while reducing processing time and increasing productivity.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a method for the synthesis of energetic thermoplastic elastomers that addresses the aforementioned problems associated with the related art and realizes the advancement expressed above.

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In accordance with the principles of this invention, these and other objects are attained by a method of synthesizing an energetic thermoplastic elastomer binder that is in a solid state at room temperature and is derived from A blocks which are crystalline at temperatures below about 60°C and B blocks are amorphous at temperatures above about -20°C. The A blocks may include one or more polyethers derived from monomers of oxetane derivatives and/or tetrahydrofuran derivatives. The B blocks may include one or more polyethers derived from monomers of oxetane and its derivatives, tetrahydrofuran and its derivatives, and/or oxirane and its derivatives. The polyoxetane blocks A and polyoxirane blocks B may be linked by end-capping the blocks with diisocyanates and linking the end-capped blocks with difunctional linking chemicals in which each of the two terminal functional groups are reactive with an isocyanate moiety of the diisocyanate.

In accordance with one embodiment of this method, the A and B blocks are dissolved into solution comprising one or more non-halogenated solvents. The solvent or solvents selected preferably are capable of dissolving more than 25% by weight of the blocks (based on total weight of the solvents and blocks) into solution, more preferably at least 35% by weight into solution, and still more preferably 50% by weight into solution. The solvents preferably do not interfere with the end capping

and ketones. Tetrahydrofuran is the preferred solvent because of its excellent solubility. The A and B blocks are mixed together at approximately the stoichiometric ratios that the blocks are intended to be present in the energetic thermoplastic elastomer. The solution is then dried by azeotropic removal of water with excess solvent. The A and B blocks are end-capped in the solvent with one or more diisocyanates. The end-capping may be performed prior or subsequent to the mixing step, but subsequent to the drying step. The diisocyanate preferably has one isocyanate moiety which is more reactive, preferably at least about five times as reactive, with the terminal hydroxyl group of each of the blocks than the other isocyanate moiety, whereby the more reactive isocyanate moiety tends to react with the terminal-hydroxyl groups of the blocks, leaving the less reactive isocyanate moiety free and unreactive. The mixture is reacted with a chain extender having two isoyanate-reactive groups that are sufficiently unhindered to react with the free and unreacted isocyanate groups of the end-capped blocks. In this manner, the end-capped blocks are linked, but not crosslinked, to form a thermoplastic elastomer.

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It is still a further object of this invention to provide a method for making propellants, especially rocket propellants and gun propellants, explosives, gas generants, or the like containing an energetic thermoplastic elastomer binder by procedures including the above-discussed method.

These and other objects, features, and advantages of the present invention will become apparent from the accompanying drawings and following detailed description which illustrate and explain, by way of example, the principles of this invention.

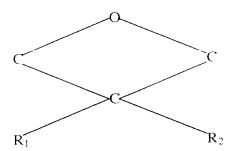
BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings are provided to facilitate an understanding of the principles of this invention. In such drawings, FIGS. 1 and 2 are graphs showing the properties of a thermoplastic elastomer prepared in accordance with an embodiment

DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic elastomer (AB)_n polymers of this invention include A blocks which are crystalline at temperatures below about 60°C, preferably at temperatures below about 75°C, and B blocks which are amorphous at temperatures down to about -20°C. Each of the A and B blocks are polyethers derived from cyclic ethers. Specifically, the A blocks are derived from monomers of oxetane derivatives and/or THF derivatives. The B blocks are derived from monomers of oxetane and its derivatives, THF and its derivatives, and/or monomers of oxirane and its derivatives, preferably energetic oxirane derivatives. The polymers melt at temperatures between about 60°C and about 120°C, and more preferably between about 75°C and about 100°C. The A and B blocks are mutually miscible in the melt. Consequently, the melt viscosity of the block copolymer decreases rapidly as the temperature is raised above the melting point, whereby high energy formulations may include high solids content, e.g., up to about 95% by weight of solid particulates, and can be easily processed. The invention also includes other thermoplastic elastomer block structures, such as ABA tri-block polymers and A_nB star polymers. Contributing to the miscibility of the A and B blocks is their similar chemical structure.

Oxetane monomer units that may be used in forming the A and B blocks of the present invention have the general formula:



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wherein the R_1 and R_2 groups are the same or different and are selected from moieties having the general formula: $-(CH_2)_nX$, where n is 0-10 and X is selected from the group consisting of -H, -NO₂, -CN, -Cl, -F, -O-alkyl, -OH, -I, -ONO₂, -N(NO₂)-alkyl, -C=CH, -Br, -CH=CH(H or alkyl), -CO₂-(H or alkyl), -N(H or alkyl)₂, -O-(CH₂)₁₋₅-O-(CH₂)₀₋₈-CH₃, and N₃.

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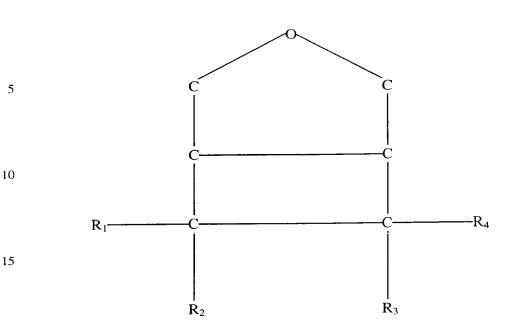
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Examples of oxetane derivatives that may be used in forming the A blocks in accordance with this invention are generally symmetrically-substituted oxetanes including, but are not limited to, the following: BEMO (3,3-6) (bis(ethoxymethyl)oxetane), BCMO (3,3-6) (bis(ethoxymethyl)oxetane), BCMO (3,3-6) (fluoromethyl)oxetane), BMMO (3,3-6) (fluoromethyl)oxetane), BAOMO (3,3-6) (interaction of the following: BEMO (3,3-6) (fluoromethyl)oxetane), BMEMO (3,3-6) (interaction of the following: BEMO (3,3-6) (fluoromethyl)oxetane), BMEMO (3,3-6) (interaction of the following: BEMO (3,3-6) (interacti

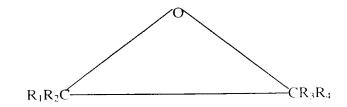
Examples of oxetanes derivatives that may be used in forming the B blocks in accordance with this invention are generally unsymmetrically-substituted oxetanes including, but are not limited to, the following: HMMO (3-hydroxymethyl-3-methyloxetane), OMMO (3-octoxymethyl-3-methyloxetane), CMMO (3-chloromethyl-3-methyloxetane), AMMO (3-azidomethyl-3-methyloxetane), IMMO (3-iodomethyl-3-methyloxetane), PMMO (3-propynomethylmethyloxetane), NMMO (3-nitratomethyl-3-methyloxetane), and MNAMMO (3-methylnitraminomethyl-3-methyloxetane).

Tetrahydrofuran monomer units that may be used in forming the blocks of the present invention have the general formula:



wherein the R₁-R₄ groups are the same or different and are selected from moieties set forth above in connection with the description of suitable oxetane derivatives.

Oxirane monomer units used in forming the B blocks of the present invention have the general formula:



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wherein R_1 and R_3 are independently selected from hydrogen and methyl, and R_2 and R_4 are independently selected from hydrogen, alkyl containing from 1 to 10 carbon atoms, chloroalkyl and bromoalkyl containing 1 to 2 carbon atoms, and nitratoalkyl, nitroalkoxyalkyl, nitroalkoxyalkyl, azidoalkyl, azidoalkoxyalkyl,

fluoronitroalkyl, and fluoronitroalkyoxyalkyl containing 1 to 5 carbon atoms provided that at least one of R_1 to R_4 is not hydrogen.

Examples of energetic oxiranes that may be used in forming the B blocks in accordance with this invention include, but are not limited to glycidyl azide polymers $(C_3H_5N_3O)$ (GAP), especially difunctional GAP, and poly(glycidyl nitrate) $(C_3H_5NO_4)$ (PGN). These polymers have a glass transition temperature below about -20° C and are amorphous at temperatures above -20° C.

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Forming thermoplastic elastomers in accordance with the invention involves (1) formation of at least one polyether-derived homopolymer, copolymer, or terpolymer serving as the A blocks and crystalline in nature with a relatively elevated melting point, i.e., between about 60°C and about 120°C, preferably near 80°C and (2) formation of at least one polyether-derived homopolymer, copolymer, or terpolymer serving as the B blocks and amorphous in structure with a glass transition temperature (T_g) below about -20°C.

The selection of the A block may be made based on the properties desired for the intended application of the thermoplastic elastomer. Examples of preferred crystalline A blocks include blocks possessing high energy density, such as those formed from BAMO and/or BMNAMO monomers. Melting temperature and ether oxygen content are additional factors that may be taken into consideration in selecting the monomers.

The properties of the block polymer depends upon the molecular weights of the individual blocks and the total molecular weights. Typically the A blocks have number average molecular weights ranging from about 3000 to about 8000, whereas the B blocks have number average molecular weights ranging from about 3000 to about 15,000. The weight ratio of A blocks to B blocks is preferably between about

15:85 to about 40:60. The preferred sizes of the A and B blocks for any particular binder application may be empirically determined.

The thermoplastic elastomers of this invention preferably are in a solid state at room temperature, have a weight average molecular weight of at least 40,000, more preferably at least 60,000, still more preferably at least 80,000, and a number average molecular weight of at least 10,000, more preferably at least 12,000, still more preferably at least 15,000.

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Thermoplastic elastomers produced in accordance with the present invention may be admixed with other components of a high energy formulation, such as a propellant formulation. The binder system, in addition to the thermoplastic elastomers, may optionally contain one or more plasticizers for improving the resistance of the thermoplastic elastomer to hardening at low temperatures, which may be included at a plasticizer-to-thermoplastic elastomer weight ratio of up to about 1:1. Suitable high energy plasticizers include glycidyl azide polymer (GAP), nitroglycerine, butanetriol trinitrate (BTTN), alkyl nitratomethyl nitramines, trimethylolethane trinitrate (TMETN), diethylene glycol dinitrate, triethylene glycol dinitrate (TEGDN), bis(dinitropropylacetal/-bis(dinitropropyl)formal (BDNPA/F), and mixtures thereof. Inert plasticizers can also be used. Representative inert plasticizers include, by way of example, dioctyladipate (DOA), isodecylperlargonate (IDP), dioctylphthalate (DOP), dioctylmaleate (DOM), dibutylphthalate (DBP), oleyl nitrile, triacetin, and combinations thereof. The binder system may also contain a minor amount of a wetting agent or lubricant that enables higher solids loading.

The solids content of the high energy composition generally ranges from about 50 wt% to about 95 wt%, higher solids loading generally being preferred so long as such loading is consistent with structural integrity. The solids include fuel material particles and powders (collectively referred to herein as particulates), such as

aluminum, magnesium, boron, and beryllium. Representative oxidizers and cooxidizers include ammonium perchlorate; hydroxylammonium nitrate (HAN);
ammonium dinitramide (ADN); hydrazinium nitroformate; ammonium nitrate;
nitramines such as cyclotetramethylene tetranitramine (HMX) and cyclotrimethylene
trinitramine (RDX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane or 2,4,6,8,10,12hexanitrohexaazaisowurtzitane (CL-20 or HNIW), and/or 4,10-dinitro-2,6,8,12tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9},0^{3,11}]dodecane (TEX), and any combination
thereof. In addition, the high energy composition may include minor amounts of
additional components known in the art, such as bonding agents, burn rate modifiers,
ballistic modifiers (e.g., lead), etc.

The thermoplastic elastomer may be mixed with the solids and other components of high energy formulation at temperatures above its melting temperature. Blending may be done in conventional mixing apparatus. Because of the low viscosities of the molten polymer, no solvents are required for blending or other processing, such as extrusion.

An important advantage of having a binder which is meltable is that the elastomer from an outdated device containing can be melted down and reused. At the time of such remelting, the binder might be reformulated, e.g., by addition of additional fuel or oxidizer particulates. Accordingly, the thermoplastic elastomer provides for its eventual recycle, as opposed to the burning required for disposal of cross-linked compositions. Because the "pot life" of the thermoplastic propellant exceeds that which would reasonably be required of a propellant or explosive formulation, if any problems develop during casting, the process can be delayed as long as is reasonably necessary, merely by maintaining the formulation in a molten state.

The oxetane homopolymer blocks may be formed according to the cationic polymerization technique taught by Manser in U.S. Patent No. 4,393,199, the complete disclosure of which is incorporated herein by reference. The oxirane homopolymer blocks may be formed according to the technique taught in U.S. Patent No. 5,120,827, the complete disclosure of which is incorporated herein by reference. The technique employs an adduct of a substance such as a diol, e.g., 1,4-butane diol (BDO), and a catalyst for cationic polymerization, e.g., BF₃-etherate. This adduct forms with the oxetane monomer an initiating species which undergoes chain extension until n moles of monomer have been incorporated in the molecule, n being the ratio of monomers to adduct present. By adjusting the ratio of monomers to adduct present, the average molecular weight of the polymer which forms may be adjusted. If two or more monomers are present, incorporation of the monomers will be generally random but may depend upon the relative reactivities of the monomers in the polymerization reaction.

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Another suitable catalyst system includes co-catalytically effective quantities of one or more triethoxonium salts and one or more alcohols, as disclosed in U.S. Application No. 08/233,219, the complete disclosure of which is incorporated herein by reference to the extent that the disclosure is compatible with this invention. Examples of triethoxonium salts include triethoxonium hexafluorophosphate, triethoxonium hexafluoroantimonate, and triethoxonium tetrafluoroborate.

It is understood that although the isocyanate-reactive terminal functional groups of the blocks are referred to herein as being hydroxyl groups, the isocyanate-reactive functional groups may also be amines, amides, and/or carboxyl groups.

The crystalline polyoxetane A blocks and amorphous B blocks, i.e., the respective prepolymers, are each end-capped together or separately with one or more diisocyanates. The end-capped A and B blocks are mixed together and joined by a

sufficiently unhindered to allow them to react with the free isocyanate moieties of the end-capped copolymers and thereby join the blocks together.

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Oxetane, THF, and oxirane polymer blocks normally have terminal isocyanate-reactive (e.g., hydroxyl) functions which are end-capped with the diisocyanates in accordance with the invention. Preferably, a first one the isocyanate moieties of the end-capping compound is substantially more reactive with the terminal-hydroxyl moieties of the polymer blocks than the other (e.g., second) isocyanate moiety. One of the problems with linking these types of polymer blocks is that substituted oxetane-derived hydroxyl end groups units have neopentyl structures, whereby the terminal primary hydroxyl moieties are substantially hindered and therefore less reactive. The blocks derived from the oxirane derivatives are secondary alcohols, making their hydroxyl groups less reactive than the primary hydroxyl group of the oxetane-derived A-block. The diisocyanate preferably is selected so that one of the isocyanate groups is capable of reacting with a hydroxyl-group of the polymer blocks while the other isocyanate moiety remains free and unreacted. Diisocyanates are preferably used because isocyanates of higher functionality would result in undesirable levels of cross-linking. The different reactivities of the isocyanate moieties is desirable to ensure that substantial chain extension through linking of like blocks does not occur. Thus, for purposes of this invention, one isocyanate moiety of the diisocyanate should preferably be approximately five times more reactive with terminal hydroxyl groups of oxetane and oxirane blocks than the other group. Preferably one isocyanate moiety is at least about ten times more reactive than the other.

One diisocyanate which is especially useful for purposes of the invention is 2,4-toluene diisocyanate (TDI) in which the isocyanate moiety in the 4-position is substantially more reactive with hindered terminal hydroxyl moieties than the isocyanate moiety in the 2-position. Isophorone diisocyanate (IPDI) is suitable for

not worked well include diphenylmethylene diisocyanate (MDI) and hexamethylene diisocyanate (HDI).

In the end-capping reaction, the diisocyanate is used at an approximately stoichiometric molar amount relative to terminal hydroxyl groups on the polymer chain. Thus, if the polymer chain has a pair of terminal hydroxyl groups, approximately two molar equivalents, e.g., 1.75-2.2 molar equivalents of diisocyanate are used. In the ideal reaction, all of the more reactive isocyanate moieties would react with terminal hydroxyl groups, leaving all of the less reactive isocyanate moieties free. Practically, not all of the diisocyanate reacts in this manner, and some chain extension does occur. Thus, the end-capping reaction may be maximized for particular polymer chains by some adjustment in the relative molar ratios of polymer block and diisocyanate.

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In one variant embodiment, the A blocks and B blocks are reacted separately with the diisocyanate, so that there is no competition of the blocks for diisocyanate molecules and each separate end-capping reaction may be carried to substantial completion. The diisocyanate may react more rapidly with one block than the other, but this difference can be compensated for by a longer reaction time with the slower reacting block. The reactivity of the terminal hydroxyl groups varies according to steric factors and also according to side-chain moieties. Energetic oxetanes, for example, generally have side-chain moieties that are electron-withdrawing, making their terminal hydroxyl groups less reactive. Once end-capped with diisocyanate, the reactivities of the polymers for linking purposes is essentially dependent only upon the reactivity of the free isocyanate, not on the chemical makeup of the polymer chain itself. Thus end-capped (A) blocks are substantially as reactive as end-capped (B) blocks.

The end-capping reaction is promoted by a suitable urethane catalyst. A

preferably two labile groups, such as chloride or acetate, bound directly to the tin. Suitable tin catalyst include diphenyl tin dichloride, dibutyl tin dichloride, dibutyl tin diacetate. Tertiary amine catalysts may also be used.

The linking compound is one which has two functional groups which are sufficiently unhindered to react with the free isocyanate moieties on the end-capped blocks so as to link A blocks to B blocks, A blocks to A blocks, and B blocks to B blocks in a urethane reaction. Preferred functional groups are hydroxyl groups, although amine, amide, and carboxyl groups, and mixtures thereof also react in a urethane reaction. Primary functional groups are preferred. The linking compound may be a short, straight carbon chain having terminal hydroxyl groups, e.g., 1,4-butanediol, 1,3-propanediol, ethylene glycol, and 1,6-hexanediol. The linking compound should also be missible with and rapidly dissolve in the non-halogenated solvent so as to ensure chain extension without unwanted amounts of cross-linking.

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Alternatively, the linking compound may be an oligomer, especially a urethane oligomer, having two functional groups which are sufficiently unhindered to react with the free isocyanate moieties on the end-capped blocks so as to link A blocks to B blocks, A blocks to A blocks, and B blocks to B blocks via a urethane reaction. Preferred functional groups of the oligomer are hydroxyl groups, although amine, amide, and carboxyl groups, and mixtures thereof also react in a urethane reaction. Primary functional groups are preferred.

An oligomeric glycol containing urethane moieties is preferably used to react the free isocyanate moieties on the end-capped blocks. The oligomeric glycol may be prepared from a mixture of one or more diisocyanates and an excess amount of one or more diols. The diisocyanate(s) and diol(s) selected and the ratio of these reagents may be varied to tailor the properties of the thermoplastic elastomer. The diol-to-diisocyanate molar ratio is preferably selected to be between 5:1 to 5:4, more

linking of the isocyanate-capped prepolymers, and improve the thermomechanical properties of the final thermoplastic elastomer. A suitable urethane reaction catalyst promotes the reaction between the diisocyanate(s) and diol(s) to form oligomers. The catalysts discussed above in connection with the linking of the A and B blocks are suitable for this purpose. Representative diols that may be selected for preparing the difunctional oligomer include, by way of example, unbranched aliphatic diols having 2 to 7 carbon atoms, such as ethylene glycol, propylene glycol, butylene glycol; and cycloaliphatic diols such as 1,4-cyclohexanedimethanol, and any combination thereof. Representative diisocyanates for preparing the difunctional oligomer include, by way of example, aliphatic diisocyanates such as hexane diisocyanate, and aryl diisocyanates such as methylene-bis(4-phenyl isocyanate), phenylene diisocyanate, toluene diisocyanate, and xylylene diisocyanate, and any combination thereof. Preferably, the difunctional oligomer has a number average molecular weight M_n of from 350 to 900.

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It is to be appreciated that a wide variety of difunctional compounds maybe used to link the end-capped blocks.

As in the end-capping reaction, some solvent is preferably used, as is a catalyst, such as described above. Conveniently, the reaction mixtures of the A blocks and B blocks may be mixed together without prior separation of the blocks from their respective end-capping reaction mixtures. The linking compound can be added directly to this mixture of A and B blocks. The catalyst is thereby already present when the linking compound is added.

The linking compound is added in an amount such that the total number of linking-compound functional groups approximately equals the total number of free isocyanate groups of the end-capped polymer blocks. Thus, to provide an (AB)_n polymer with multiple blocks in each chain, the linking compound to polymer block

molar ratio is in the range of 0.9-1.1, e.g., 1.0. Accordingly, optimal molar ratios of blocks and linking chemicals may have to be empirically determined.

The end-capping reaction and linking reaction are carried out in a suitable non-halogenated solvent, e.g., one which dissolves the polymer and does not react with the free isocyanate moieties. Although insubstantial amounts of halogenated solvent may be present, the solution is preferably completely free of any halogenated solvent. The non-halogenated solvent should not react in the urethane reaction and forms an azeotrope with water. Suitable dry solvents include cyclic ethers such as tetrahydrofuran (THF) and 1,4-dioxane; non-cyclic ethers such as ethylene glycol dimethyl ether; ketones such as methyl ethyl ketone ("MEK"); and esters such as cthyl acetate. Of these, THF is preferred because of its excellent solubility characteristics.

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In a preferred embodiment, the solvent forms an azeotrope with water. In this preferred embodiment, after the blocks are dissolved in excess non-halogenated solvent, the solution may be dried by azeotropic distillation of the solvent, and optionally further concentrated, e.g., via distillation, in the solution to increase the volumetric loading and reaction rate. The blocks then may be end-capped, separately or together, and linked in the same or a different non-halogenated solvent. By distilling off excess solvent to remove water, subsequent reaction with a diisocyanate may proceed without significant interference from competing reactions between the isocyanate moieties and water. Additionally, the solution remains homogeneous and further distillation serves to concentrate the polymer solution, producing higher reaction rates and requiring less reactor capacity. The reaction rates may be improved by conducting the end-capping reaction at elevated temperatures, such as 30°C to 80°C, more preferably 40°C to 60°C. The process may be conducted by a batch or continuous method. For example, the prepolymer and catalyst solution may be continuously fed through a mixer/extruder into which is injected a diisocyanate and a diol at appropriate rates and positions so that urethane linking occurs within the

extruder and energetic thermoplastic elastomer is continuously produced for processing.

In the end-capping and block linking steps, the reaction can be followed with NMR and IR. With NMR, the urethane-forming reaction can be followed through the methylene groups on the polymer adjacent to the terminal hydroxyl groups. With IR, the change from isocyanate to urethane can be directly followed.

Synthesis of polyoxetanes is described in U.S. Patent Nos. 4,483,978 and 4,806,613, the complete disclosures of which are incorporated herein by reference to the extent that these disclosures are compatible with the present invention.

The invention will now be described in greater detail by way of the following examples, which are not to be construed as exhaustive as to the scope of this invention.

As referred to herein, "dry" means that less than 1 wt% water was present.

For the following experiments, poly(azidomethyloxirane) was supplied by 3M Speciality Chemicals of St. Paul, MN (Lot L-12564). Unless otherwise specified, all other materials were obtained from Aldrich of Milwaukee, WI.

EXAMPLE 1 (poly(3,3-bis(azidomethyl)oxetane))

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A 5 liter jacketed flask equipped with a mechanical stirrer was charged with 600 grams of tribromoneopentylalcohol (AmeriBrom, Inc. of New York), 1200 ml of toluene, and 6 grams of tetrabutylammonium bromide. The mixture was cooled to 12°C and 193 grams of sodium hydroxide was added dropwise as a 40 wt% solution keeping the temperature at 12°C. After 36 hours the reaction mixture was washed with water until the pH was less than 9 to obtain the crude product which was distilled to obtain 3,3-bis(bromomethyl)oxetane at 65% yield.

A 5 liter jacketed flask equipped with a mechanical stirrer was charged with 1450 grams of the 3,3-bis(bromomethyl)oxetane and 1720 ml of toluene. The mixture was stirred and heated to 60°C before 1600 ml of water, 14.7 grams of tetrabutylammonium bromide, and 862 grams of sodium azide were added. After 24 hours, the reaction mixture was cooled to room temperature and washed three times with 2000 ml of water. The toluene and water were removed from the organic layer by distillation to give pure 3,3-bis(azidomethyl)oxetane at 85% yield.

Under an argon atmosphere, 14.94 grams of butane diol was added to a flame dried 5 liter round-bottomed flask charged with 1340 ml of dry methylene chloride. To this mixture, 11.77 grams of borontrifluoride-etherate was added and the reaction was allowed to proceed for one hour at room temperature. The reactor was then cooled to -10°C and 937.78 grams of the 3,3-bis(azidomethyl)oxetane was added. The solution was allowed to come to room temperature and left to react for three days. The reaction was then quenched by the addition of 50 ml of saturated brine solution. The organic phase was separated off and washed with 100 ml of 10 wt% sodium bicarbonate solution before the solvent was removed on a rotovapor. The resulting liquid was then poured into 5 liters of methanol to precipitate the polymer, which was filtered from the solution and dried under vacuum at 30°C.

EXAMPLE 2 (poly(3-azidomethyl-3-methyloxetane))

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A 5 liter jacketed flask equipped with a mechanical stirrer was charged with 1062 grams of sodium azide, 1972 ml of water, and 2450 grams of 3-bromomethyl-3-methyloxetane (supplied by AmeriBrom, Inc. of New York). This mixture was brought to reflux with vigorous mixing. After 48 hours the mixture was cooled to room temperature. The organic layer was separated off and washed three times with 1000 ml of water before being dried over molecular sieves to yield pure 3-azidomethyl-3-methyloxetane at 85% yield.

Under an argon atmosphere, 14.94 grams of butane diol was added to a flame dried 5 liter round-bottomed flask charged with 1.340 ml of dry methylene chloride. To this mixture, 11.77 grams of borontrifluoride-etherate was added and the reaction was allowed to proceed for one hour at room temperature. The reactor was then cooled to -10°C and 937.78 grams of the 3-azidomethyl-3-methyloxetane was added. The solution was allowed to come to room temperature and left to react for three days. The reaction was then quenched by the addition of 50 ml of saturated brine solution. The organic phase was separated off and washed with 100 ml of 10 wt% sodium bicarbonate solution before the solvent was removed on a rotovapor. The resulting liquid was then poured into 5 liters of methanol to precipitate the polymer, which was filtered from the solution and dried under vacuum at 30°C.

EXAMPLE 3 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) in THF)

In a one liter round bottom flask, 65 grams of dry difunctional poly(3-azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3121 and 35 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3235 were dissolved in 650 grams of dry tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran under reduced pressure via a rotovapor until 100 grams of the solvent remained. To this solution, 0.1 grams of diphenyltin dichloride and 5.41 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic stirrer at ambient temperature and pressure. After 24 hours, 1.40 grams of butane-1,4-diol was added causing the solution to become steadily more viscous. After another 24 hours, the solution was poured into methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties set forth below:

Mn = 20480

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Mw/Mn = 5.9

 $E^{1.0}$ (psi) = 754

 $\varepsilon_{\rm m} \, (\%) = 204$

 ε_f (failure) (%) = 229

 $5 \qquad \sigma_{\rm m} \, (\rm psi) = 180$

 $\sigma_{\rm m}$ (corrected) (psi) = 558

Shore A = 64

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EXAMPLE 4 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) in THF)

In a 100 ml round bottom flask, 6.5 grams of dry difunctional poly(3-azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3040 and 3.5 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3235 were dissolved in 60 ml of dry tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran under reduced pressure via a rotovapor until 10 grams of the solvent remained. To this solution, 0.25 ml of dibutyltin dilaurate and 0.561 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic stirrer at ambient temperature and pressure. After 15 minutes, 0.145 grams of butane-1,4-diol was added causing the solution to become steadily more viscous. After another 30 minutes, the solution was poured into methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties set forth below:

Mn = 15404

Mw = 67277

25 Mw/Mn = 4.37

EXAMPLE 5 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) in 1,4-dioxane)

azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3040 and 3.5 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3235 were dissolved in 60 ml of dry 1,4-dioxane. The solution was concentrated and dried by evaporation of the 1,4-dioxane under reduced pressure via a rotovapor until 12 grams of the solvent remained. To this solution, 0.3 ml of dibutyltin dilaurate and 0.561 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic stirrer at ambient temperature and pressure. After one hour, 0.145 grams of butane-1,4-diol was added causing the solution to become steadily more viscous. After another two hours, the solution was poured into methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times

The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties set forth below:

Mn = 21230

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Mw = 116272

15 Mw/Mn = 5.48

EXAMPLE 6 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) in ethyl acetate)

In a 500 ml round bottom flask, 18 grams of dry difunctional poly(3-azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3356 and 6 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3235 were dissolved in 200 ml of dry ethyl acetate. The solution was concentrated and dried by evaporation of the ethyl acetate under reduced pressure via a rotovapor until 34 grams of the solvent remained. To this solution at 40°C, 0.024 grams of diphenyltin dichloride and 1.26 grams of toluene-2.4-diisocyanate were added while stirring with a magnetic stirrer. After one hour, 0.33 grams of butane-1,4-diol was added causing the solution to become steadily more viscous. After another 48 hours, the solution was poured into methanol in a volume ratio of 1:5. The methanol was

methanol (1:5 volume ratio) to give a rubbery granular product with the properties set forth below:

Mn = 13880

Mw = 43310

5 Mw/Mn = 3.12

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EXAMPLE 7 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) in THF)

In a 100 ml round bottom flask, 6.5 grams of dry difunctional poly(3-azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3040 and 3.5 grams of dry poly(3,3 bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3235 were dissolved in 70 ml of dry tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran under reduced pressure via a rotovapor at 50°C until 5 grams of the solvent remained. To this solution at 50°C, 0.5 ml of dibutyltin dilaurate and 0.561 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic stirrer. After three minutes, 0.145 grams of butane-1,4-diol was added causing the solution to become steadily more viscous. After another five minutes, the solution was diluted with 20 ml of tetrahydrofuran and 1 ml of methanol. This solution was then precipitate in methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties set forth below:

Mn = 17350

Mw = 103231

Mw/Mn = 5.95

EXAMPLE 8 (Random block copolymer of poly(azidomethyloxirane) and poly(3,3-bis(azidomethyl)oxetane))

In a 25 ml round bottom flask, a urethane oligomer was prepared by dissolving

solution 0.1 ml of dibutyltin dilaurate followed by 1.60 grams of butane-1,4-diol. This reaction mixture was stirred for 1 hour at room temperature.

In a separate 250 ml round bottom flask, 17.94 grams of dry difunctional poly(azidomethyloxirane) with a hydroxyl equivalent weight of 1174 and 6.63 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 2390 were dissolved in 100 ml of dry tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran under reduced pressure via a rotovapor until 20 grams of the solvent remained. To this solution, 75 ml of dibutyltin dilaurate and 3.097 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic stirrer at ambient temperature and pressure. After one hour, the urethane oligomer was added to this solution, causing the solution to become steadily more viscous. After 20 minutes, the solution was too viscous to stir and was diluted with 20 ml of dry tetrahydrofuran and allowed to react for a further 20 minutes before being poured into methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties shown in FIGS. 1 and 2 and set forth below:

Mn = 26240

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Mw = 175500

20 Mw/Mn = 6.69

Molecular weight distribution was determined by gel permeation chromotography using polystyrene standards, with the results shown in FIG. 1. The GPC trace in FIG. 1 demonstrates that the prepolymers were linked to produce a copolymer having a higher molecular weight and dispersivity than the homopolymer blocks. The DMA trace in FIG. 2 shows the melt transition of random block (BAMO-GAP)_n at 75-80°C with a material modululs reducing only slowly before this point.

EXAMPLES 9-11 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) linked with a urethane oligomer)

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In a 500 ml round bottom flask, 45 grams of difunctional poly(3-azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3125 and 15 grams of poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3152 were dissolved in 300 ml of tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran or a rotovapor until a solution with 90 grams of solvent remained. To this solution 0.6 grams of dibutyltin dichloride and 3.34 grams of toluene-2,4-diisocyanate was added and the mixture allowed to react for 3 hours to end-cap the prepolymer.

For Example 9, 0.22 grams of butanediol was added to one quarter of the isocyanate end-capped prepolymer mixture. The reaction was allowed to continue for 14 hours before it was precipitated with methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product.

For Example 10, a urethane oligomer was derived from a mixture of 2 ml of tetrahydrofuran, 0.42 grams of toluene-2,4-diisocyanate, 0.43 grams of butane-1,4-diol, and 0.1 grams of dibutyltin dichloride, which were allowed to react for one hours. The urethane oligomer was then added to one quarter of the isocyanate end-capped prepolymer mixture and allowed to react for 14 hours before it was precipitated with methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product.

For Example 11, a urethane oligomer was derived from a mixture of 2 ml of tetrahydrofuran, 0.83 grams of toluene-2,4-diisocyanate, 0.65 grams of butane-1,4-diol, and 0.1 grams of dibutyltin dichloride, which were allowed to result for one

hours. The urethane oligomer was then added to one quarter of the isocyanate end-capped prepolymer mixture and allowed to react for 14 hours before it was precipitated with methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product.

TABLE

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	Example 9	Example 10	Example 11
diol:diisocyanate	1:0	2:1	3:2
molar ratio			
Mn	11440	12340	13240
Mw	134800	142000	122600
Mw/Mn	11.78	11.51	9.26
$E^{1.0}$	520	669	823
ε _m (%)	311	897	536
ε _f (failure) (%)	372	1082	562
σ _m (psi)	153	345	300
σ _m (corrected) (psi)	678	3575	2381
ShoreA	49	60	65

The foregoing detailed description of the preferred embodiments of the invention has been provided for the purpose of explaining the principles of the invention and its practical application, thereby enabling others skilled in the art to understand the invention for various embodiments and with various modifications as are suited to the particular use contemplated. The foregoing detailed description is not intended to be exhaustive or to limit the invention to the precise embodiments disclosed. Modifications and equivalents will be apparent to practitioners skilled in this art and are encompassed within the spirit and scope of the appended claims.

WHAT IS CLAIMED IS:

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- 1. A method of preparing a thermoplastic elastomer having A blocks which are crystalline at temperatures below about 75°C and the B blocks which are amorphous at temperatures above about -20°C, the method comprising:
- (a) dissolving the A blocks and B blocks terminated with respective isocyanate-reactive groups at approximately the stoichiometric ratios that are intended to be present in the thermoplastic elastomer into solution comprising at least one non-halogenated solvent, the A blocks being crystalline at temperatures below about 75°C and derived from monomers comprising at least one member selected from the group consisting of oxetane derivatives and tetrahydrofuran derivatives, the B blocks being amorphous at temperatures above about -20°C and derived from monomers comprising at least one member selected from the group consisting of oxetane and derivatives thereof, tetrahydrofuran and derivatives thereof, and oxirane and derivatives thereof;
- (b) drying the dissolved A blocks and B blocks of water by azeotropic distillation of the non-halogenated solvent;
- (c) end-capping the dried A blocks and the dried B blocks in the non-halogenated solvent by reacting the dried A blocks and the dried B blocks with at least one diisocyanate in which a first isocyanate moiety thereof is substantially more reactive with the terminal groups of the blocks as a second isocyanate moiety thereof, whereby the more reactive first isocyanate moiety is capable of reacting with the terminal groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted; and
- (d) linking the end-capped A blocks and the end-capped B blocks together in the non-halogenated solvent with at least one linking compound comprising two isocyanate-reactive groups which are sufficiently sterically unhindered to react with the free and unreacted isocyanate moieties of the end-capped polymers.

- 2. A method as defined in claim 1, wherein said dissolving step (a) comprises separately dissolving the A blocks and the B blocks into respective solutions.
- 3. A method as defined in claim 2, wherein said end-capping step (c) comprises separately end-capping the A blocks and the B blocks in the respective solutions.
 - 4. A method as defined in claim 1, wherein said steps (a), (b), (c), and (d) are conducted in the absence of any halogenated solvent.
- 5. A method as defined in claim 1, wherein the non-halogenated solvent comprises one or more organic ethers.
 - 6. A method as defined in claim 5, wherein the organic ether comprises one or more members selected from the group consisting of tetrahydrofuran, ethylene glycol dimethyl ether, and 1,4-dioxane.
- 7. A method as defined in claim 6, wherein the organic ether comprises tetrahydrofuran.
 - 8. A method as defined in claim 1, wherein the non-halogenated solvent comprises one or more organic esters.
 - 9. A method as defined in claim 8, wherein the organic ester comprises ethyl acetate.
 - 10. A method as defined in claim 1, wherein the non-halogenated solvent comprises one or more organic ketones.
 - 11. A method as defined in claim 10, wherein the organic ketone comprises methyl ethyl ketone.

- 12. A method as defined in claim 1, wherein the linking compound is derived from at least one diisocyanate and at least one difunctional urethane oligomer comprising two functional groups which are reactive with isocyanate moieties of the diisocyanate.
 - 13. A method as defined in claim 1, wherein:

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the first isocyanate moiety of the diisocyanate is at least five times more reactive with the terminal groups of each of the blocks as the second isocyanate moiety, whereby the more reactive first isocyanate moiety is capable of reacting with and end capping the terminal groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted; and

the linking compound has two isocyanate-reactive hydroxyl groups which are sufficiently sterically unhindered to be reactive with the free and unreacted second isocyanate groups of the end-capped blocks.

- 14. A method as defined in claim 1, wherein the diisocyanate comprises toluene diisocyanate.
 - 15. A method as defined in claim 1, wherein the thermoplastic elastomer has a weight average molecular weight of at least 40,000 and a number average molecular weight of at least 10,000.
- 16. A method as defined in claim 1, wherein the thermoplastic elastomer
 has a weight average molecular weight of at least 60,000 and a number average
 molecular weight of at least 12,000.
 - 17. A method as defined in claim 1, wherein the thermoplastic elastomer has a weight average molecular weight of at least 80,000 and a number average molecular weight of at least 15,000.

18. A method as defined in claim 1, wherein the isocyanate-reactive terminal groups of the A and B blocks are hydroxyl groups.

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- 19. A method of making an energetic composite binder comprising:
- (a) dissolving the A blocks and B blocks terminated with respective isocyanate-reactive groups at approximately the stoichiometric ratios that are intended to be present in the thermoplastic elastomer into solution comprising at least one non-halogenated solvent, the A blocks being crystalline at temperatures below about 75°C and derived from monomers comprising at least one member selected from the group consisting of oxetane derivatives and tetrahydrofuran derivatives, the B blocks being amorphous at temperatures above about -20°C and derived from monomers comprising at least one member selected from the group consisting of oxetane and derivatives thereof, tetrahydrofuran and derivatives thereof, and oxirane and derivatives thereof;
- (b) drying the dissolved A blocks and B blocks of water by azeotropic distillation of the non-halogenated solvent;
- (c) end-capping the dried A blocks and the dried B blocks in the non-halogenated solvent by reacting the dried A blocks and the dried B blocks with at least one diisocyanate in which a first isocyanate moiety thereof is substantially more reactive with the terminal groups of the blocks as a second isocyanate moiety thereof, whereby the more reactive first isocyanate moiety is capable of reacting with the terminal groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted;
- (d) linking the end-capped A blocks and the end-capped B blocks together in the non-halogenated solvent with at least one linking compound comprising two isocyanate-reactive groups which are sufficiently sterically unhindered to react with the free and unreacted isocyanate moieties of the end-capped polymers; and
 - (e) blending the thermoplastic elastomer with about 50 wt% to about 95

wt% of at least one solid selected from the group consisting of fuel material particulates and oxidizer particulates.

20. A method as defined in claim 19, wherein said dissolving step (a) comprises separately dissolving the A blocks and the B blocks into respective solutions.

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- 21. A method as defined in claim 20, wherein said end-capping step (c) comprises separately end-capping the A blocks and the B blocks in the respective solutions.
- 22. A method as defined in claim 19, wherein said steps (a), (b), (c), and (d) are conducted in the absence of any halogenated solvent.
 - 23. A method as defined in claim 19, wherein the non-halogenated solvent comprises one or more organic ethers.
 - 24. A method as defined in claim 23, wherein the organic ether comprises one or more members selected from the group consisting of tetrahydrofuran, ethylene glycol dimethyl ether, and 1,4-dioxane.
 - 25. A method as defined in claim 23, wherein the organic ether comprises tetrahydrofuran.
 - 26. A method as defined in claim 19, wherein the non-halogenated solvent comprises one or more organic esters.
- 20. A method as defined in claim 26, wherein the organic ester comprises ethyl acetate.
 - 28. A method as defined in claim 19, wherein the non-halogenated solvent comprises one or more organic ketones.

- 29. A method as defined in claim 28, wherein the organic ketone comprises methyl ethyl ketone.
- 30. A method of making a rocket motor propellant comprising making a binder as defined in claim 19.
- 31. A method of making a gun propellant comprising making a binder as defined in claim 19.

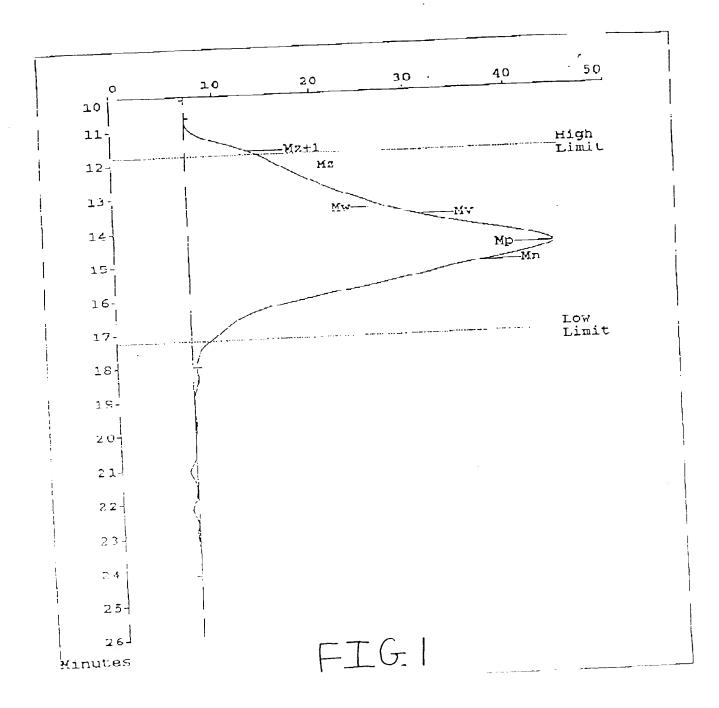
- 32. A method of making an explosive comprising making a binder as defined in claim 19.
- A method of making a gasifier comprising making a binder as defined in claim 19.

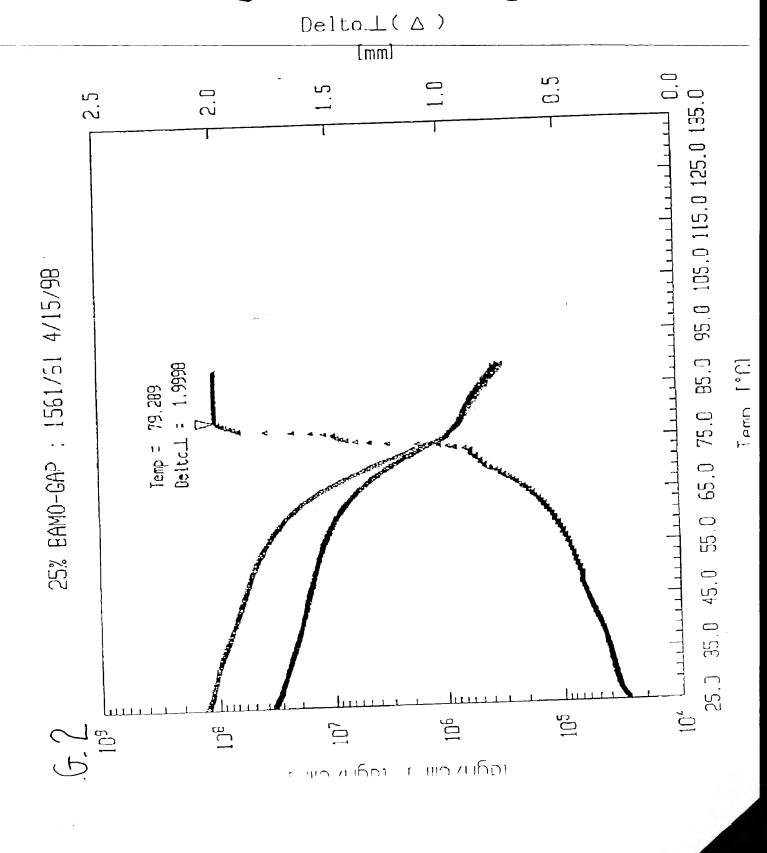
ABSTRACT OF THE DISCLOSURE

A method of preparing a thermoplastic elastomer having A blocks which are crystalline at temperatures below about 75°C and B blocks which are amorphous at temperatures above about -20°C is disclosed. The A blocks are derived from oxetane derivatives and/or tetrahydrofuran derivatives. The B blocks are derived from oxetanes, tetrahydrofuran, oxiranes, and derivatives thereof. The A blocks and B blocks are dissolved into solution containing a non-halogenated solvent, preferably tetrahydrofuran. The dissolved A blocks and B blocks are dried of water by azeotropic distillation of the non-halogenated solvent. Next, the dried A blocks and the dried B-blocks are end-capped with a diisocyanate having one isocyanate moiety substantially more reactive with the terminal groups of the blocks than the other isocyanate moiety, whereby the more reactive isocyanate moiety is capable of reacting with the terminal groups of the blocks, leaving the less reactive isocyanate moiety free and unreacted. The end-capped A blocks and the end-capped B blocks are linked together with a linking compound having two isocyanate-reactive groups which are sufficiently unhindered to react with the free and unreacted isocyanate moieties of the end-capped polymers.

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INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

COLTON, Kendrew H. PILLSBURY MADISON & SUTRO, LLP 1100 New York Avenue, N.W. Washington, D.C. 20005 **ETATS-UNIS D'AMERIQUE**

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY **EXAMINATION REPORT**

(PCT Rule 71.1)

Date of mailing (day/month/year)

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IMPORTANT NOTIFICATION

Applicant's or agent's file reference

98-33-SE PCT

PCT/US99/24013

International application No.

International filing date (day/month/year) .09/11/1999

12/11/1998

Priority date (day/month/year)

Applicant

CORDANT TECHNOLOGIES, INC. et al.

- 1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
- 2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
- 3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide



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49 89 2399 - 0 Tx, 523656 epmu di

Fax: +49 89 2399 - 4465

Hardy Maguar J. 🗽

Tel. +49 89 2399-8151



PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 98-33-SE PCT		ile reference	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IF		
International application No.		n No.	International filing date (day/month/year)		Priority date (day/month/year)
PCT/US99/24013			09/11/1999		12/11/1998
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⊠ Th be (s	nis report een amer ee Rule 7	is also accompanied and are the bas	sis for this report and/or sheets on the Administrative Instruction	e descriptio ontaining re	n, claims and/or drawings which have ectifications made before this Authority ne PCT).
3. This re	Bas□ Prio□ No□ Lac□ Recita	sis of the report ority n-establishment of o ck of unity of inventic asoned statement un	nder Article 35(2) with regard to ons suporting such statement		and industrial applicability entive step or industrial applicability;
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Fax: +49 89 2399 - 4465

Radke, M

Telephone No. +49 89 2399 8677



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US99/24010

I. Basis of	the report
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1.	resp the	This report has been drawn on the basis of (substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).): Description, pages:					
	3-8,	10-27	as originally filed				
-	1,2,	9	as received on	09/06/2000	with letter of	09/06/2000	
	Clai	ms, No.:					
	1-33	3	as originally filed				
	Drawings, sheets:						
	1/2,	2/2	as originally filed				
2.		With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.					
	These elements were available or furnished to this Authority in the following language: , which is:						
		☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).				under Rule 23.1(b)).	
		the language of pu	ublication of the international a	oplication (und	er Rule 48.3(b)).		
		the language of a 55.2 and/or 55.3).	translation furnished for the pu	rposes of inter	national preliminary e	examination (under Rule	
3.	With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:						
		contained in the in	nternational application in writte	n form.			
		filed together with	the international application in	computer read	dable form.		
		☐ furnished subsequently to this Authority in written form.					
		furnished subsequ	uently to this Authority in compl	uter readable f	orm.		
		s den eller i strig has been tu			; · · · · · · · · · · · · · · · · · · ·	in willer sedue" n	

4. The amendments have resulted in the cancellation of:

INTERNATIONAL PRELIMINARY **EXAMINATION REPORT**

International application No. PCT/US99/24013

		the description,	pages:
		the claims,	Nos.:
		the drawings,	sheets:
5.	This report has been established as if (some of) the amendments had not been made, since they have considered to go beyond the disclosure as filed (Rule 70.2(c)):		
		(Any replacement sh	eet containing such amendments must be referred to under item 1 and annexed to this

report.) see separate sheet

- 6. Additional observations, if necessary:
- V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- 1. Statement

Claims 1-33 Novelty (N) Yes:

No: Claims

Inventive step (IS) Yes: Claims 5-12 and 23-29

> No: Claims 1-4, 13-22, 30-33

Industrial applicability (IA) Yes: Claims 1-33

> Claims No:

2. Citations and explanations see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted: see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item I

Basis of the opinion

The amendments filed with the letter dated 09. 06. 2000 introduce subject-matter which extends beyond the content of the application as filed, contrary to Article 34(2)(b) PCT. The amendments concerned are the following:

The replacement of the first formula on page 9 by another one.

Both the original and the amended formula depict THF derivatives. Even if the expert might regard the original formula as being wrong, it was not immediately evident that the original formula was to be replaced by the one on amended page 9. One could also think of a formula where at least one of the radicals R₁, R₂, R₃ or R₄ is situated at a carbon atom adjacent to the oxygen of the tetrahydrofuran ring. It should be borne in mind that no specific THF derivatives are disclosed in the present application.

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Cited literature 1.

(a) Reference is made to the following documents:

D1: US-A-4 806 613 D2: US-A-5 210 153

D3: US-A-4 393 199

(c) Document D3 which is cited at 4.22-26 of the present description was not mentioned in the international search report. A copy of the document was

2. Novelty

Document **D1** is considered to represent the most relevant prior art. It describes a process (see claim 1 and examples 9 and 10) which differs from the one of the present claims in that no non-halogenated solvent is employed. In the examples CH₂Cl₂ is used as the solvent. At 8/60-62 no specific solvent is mentioned.

For this reason, the subject-matter of the present claims is novel.

3. Inventive step

- (a) The problem solved by using a non-halogenated solvent was to avoid the use of solvents that have a detrimental effect on the environment (see 4/2-3).
- (b) The use of a non-halogenated solvent for this purpose was obvious in view of **D2**, example 9. Said example mentions that benzene, dichloromethane or tetrachloroethane are useful as solvents for the soft block (e.g. BMMO/THF). In contrast to the applicant's view there is no indication in this example that dichloromethane or tetrachloroethane should be used *in lieu of* benzene. The expert thus knew that he could replace the dichloromethane employed in **D1** by benzene and thereby avoid a solvent hazardous to the ozone layer of the earth.
- (c) For this reason, the subject-matter of <u>claims 1-4, 13-22 and 30-33</u> is not deemed to be based on an inventive step.
- (d) None of the cited documents does, however, suggest to use organic ethers, actors or ketones as solvents.

solvent (see **D3**, 10/5-15), i.e. a rather exotic solvent, and

that halogenated solvents were used throughout the examples of the cited

EXAMINATION REPORT - SEPARATE SHEET

it is not deemed to be obvious to the expert to replace the solvents employed in the prior art by organic ethers, esters or ketones.

- (e) Nor is there any suggestion to use a linking component derived form at least one diisocyanate and at lest one difunctional urethane oligomer (see present claim 12).
- (f) Consequently the subject-matter of claims 5-12 and 23-29 is deemed to be inventive.

Re Item VII

Certain defects in the international application

- The terms "the complete disclosures of which are incorporated ... with this 1. invention" and the like at 3/7-9, 13/3-18 and 19/8-9) leave doubt as to the actual disclosure of the present invention. Said terms should have been deleted.
- 2. The word "about" should have been deleted in the description whenever relating to ranges mentioned in the present claims (see 5/11-12, 7/3-5+10 and 10/11-14).
- 3. The reference to the application number at 13/16-17 should have been deleted or replaced by one to the respective publication or patent number.
- The word "Preferably" should have been deleted at 14/5+16 (see claim 1). 4.
- The sentence at 14/28-15/2 should have been deleted as the NCO-groups in the 5

Re Item VIII

Certain observations on the international application

Clarity of the claims

- (a) The word "about" blurs the ranges given in <u>claims 1 and 19</u> (cf. 28/3+4+8+11 and 31/7+10+27) thus rendering these claims unclear.
- (b) The statement in the description at 27/12-15 implies that the subject-matter for which protection is sought may be different to that defined by the claims, thereby resulting in lack of clarity (Article 6 PCT) when used to interpret them (see also the PCT Guidelines, III-4.3a).
- (c) There is a discrepancy between <u>claims 1 and 19</u> (see 28/8 and 31/7: "below about 75 °C") and the description at 5/11 ("below about 60 °C) and at 7/3-4+10.

METHOD FOR THE SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS IN NON-HALOGENATED SOLVENTS

Priority is claimed on U.S. provisional application 60/108,455 filed on November 12, 1998

BACKGROUND OF THE INVENTION

1. Field of the Invention

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This invention relates to a method of synthesizing energetic thermoplastic elastomers which are useful as binders of high energy compositions, such as rocket motor propellants, gun propellants, explosive munitions, gas generants of vehicle supplemental restraint systems, or the like.

2. Description of the Related Art

Solid high energy compositions, such as propellants, explosives, gas generants, and the like comprise solid particulates, such as fuel particulates and/or oxidizer particulates, dispersed and immobilized throughout a polymeric binder matrix.

Conventional solid composite propellant binders utilize cross-linked elastomers in which prepolymers are cross-linked by chemical curing agents. As outlined in detail in U.S. Patent No. 4,361,526, there are important disadvantages to using cross-linked elastomers as binders. Cross-linked elastomers must be east within a short period of time after addition of the curative, which time period is known as the "pot life". Disposal of a cast, cross-linked propellant composition is difficult, and usually is accomplished by burning, which poses environmental problems. Furthermore, current state-of-the-art propellant compositions have serious problems that include their use of nonenergetic binders which have lower performance and high end-of-mix viscosities.

In view of the inherent disadvantages associated with the use of cross-linked elastomeric polymers as binder materials, there has been considerable interest in

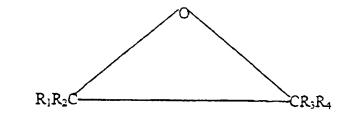
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requirements expected of propellant formulations, particularly the requirement of

wherein the R₁-R₄ groups are the same or different and are selected from moieties set forth above in connection with the description of suitable oxetane derivatives.

Oxirane monomer units used in forming the B blocks of the present invention have the general formula:



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wherein R₁ and R₃ are independently selected from hydrogen and methyl, and R₂ and R₄ are independently selected from hydrogen, alkyl containing from 1 to 10 carbon atoms, chloroalkyl and bromoalkyl containing 1 to 2 carbon atoms, and nitratoalkyl nitratoalkoxyalkyl, nitroalkoxyalkyl, azidoalkyl, azidoalkoxyalkyl,

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